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**Beach placer, a proxy for the average Nd and Hf isotopic
composition of a continental area**

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Abstract

Beach placer deposits concentrate detrital heavy minerals which are the erosion products of large areas of continental crust. Here, we report the first analyses of Nd-Hf isotopic ratios and trace element concentrations that we measured in a beach placer from Camargue, France and in its pure mineral separates. Both the bulk composition of the placer and those of its pure mineral separates were determined. We also report mineral proportions obtained using observations under a binocular microscope and micro X-ray fluorescence mapping.

Our results indicate that monazite totally controls the placer's Nd isotopic composition ($\epsilon_{Nd} = -9.3$) while zircon dominates its Hf isotopes ($\epsilon_{Hf} = -13.0$) even though both mineral phases represent only a small proportion of the heavy mineral assemblage (3.5 and 10% respectively). We demonstrate that the Camargue placer provides a good estimate of the average Nd and Hf isotopic composition of the continental area drained by the Rhone River in western Europe ($\epsilon_{Nd} \approx -9$ and $\epsilon_{Hf} \approx -13$). Using these values, we calculate two stage model ages and show that almost all the placer minerals are derived from Proterozoic crustal protoliths. This provides valuable information on the history of the continental crust drained by the Rhone River. In particular, it suggests that little juvenile crust was created during the recent geological events that formed the Alps and the Massif Central, the two main massifs from which the placer minerals originate.

More generally, we propose that similar measurements made on other worldwide beach placer deposits could provide estimates of the present-day Nd and Hf isotopic composition of large continental areas, values that are difficult to obtain due to the well-known heterogeneity of continental material but are essential to model the growth of continental crust through Earth history or to model the impact of crustal material when recycled into the mantle.

Keywords: Neodymium, hafnium, monazite, zircon, continental crust

1. Introduction

Modern beach placer deposits are surficial accumulations of clastic heavy minerals that mostly form in the foreshore of sandy beaches by gravity separation under the action of waves and currents. In some regions, beach placers contain valuable heavy minerals such as ilmenite, zircon or monazite and have been studied to identify economically viable deposits (e.g. Patyk-Kara, 2002; Levchenko, 2006; Patyk-Kara, 2008) or to better understand the mechanisms responsible for mineral sorting and depositional patterns (e.g. Komar and Wang, 1984; Frihy et al., 1995; Roy, 1999; Hughes et al., 2000; Hou et al., 2003; Paine et al., 2005). Apart from Götze and Lewis (1994) who studied a few trace elements in pure mineral fractions separated from mature quartz sands, no study has focused on the isotope and trace-element geochemistry of placers and their heavy minerals, even though this type of sediment obviously has the potential to provide valuable insights on broader issues such as fluvial transport processes, crust-mantle recycling or the composition of the upper continental crust.

Several previous studies (see for example, Goldstein and Jacobsen, 1988; Gaillardet et al., 1995; Allègre et al., 1996; Millot et al., 2004; Kamber et al., 2005) used river sediments as proxies to evaluate either the trace element content or the Nd and Pb isotopic compositions of the upper continental crust and its evolution through time. Other studies used Hf and Pb isotopes on individual zircon grains to constrain the timing of major crustal growth episodes as well as their mantle versus crustal sources (Gehrels et al., 1995; Amelin et al., 1999; Bodet and Schärer, 2000; Griffin et al., 2006; Hawkesworth and Kemp, 2006; Dhuime et al., 2011). However, no study ever considered taking advantage of the natural processes leading to the formation of zircon-rich placers to place constraints on both the composition and history of large-scale continental areas.

Here we present the first Nd and Hf isotopic analyses, as well as trace element concentrations, of several pure mineral separates that were isolated from a beach placer sampled

75 near the Rhone delta in Camargue, France. The proportion of each heavy mineral species was
76 estimated as precisely as possible using observations under a binocular microscope and micro
77 X-ray fluorescence mapping. Using all these data, we (a) quantify the influence of the individual
78 minerals on the trace element and isotopic composition of the entire placer, (b) we discuss and
79 interpret the chemical characteristics of beach placers and (c) we demonstrate that placers are
80 good proxies of the average Nd-Hf isotopic composition of large regions of the continental crust
81 exposed to weathering and erosion.

82

83 **2. Materials and Methods**

84 **2.1. Brief setting and placer sampling**

85 The studied placer was sampled in 2003 next to the Rhone River delta on the Espiguette
86 Beach in Camargue, France (see Figure 1) within the zone of wave swash where black-sand
87 deposits are regularly observed after storms. Several kilos of mature sand, rich in black heavy
88 minerals and mixed with very small proportions of light minerals, were collected using a spade
89 on the beach. Previous studies (BRGM, 2000) showed that the Espiguette black-sands usually
90 contain variable abundances of about twenty heavy minerals that are commonly found in beach
91 placer deposits. These include ilmenite, magnetite, rutile, garnet, zircon, monazite and epidote
92 (see Supplementary Table 1 for the complete list of minerals).

93 As shown in Figure 1, Espiguette beach is about 10 kilometres long and grows by
94 accumulation of sediments transported from east to west by longshore currents (Vella et al.,
95 2005; Sabatier et al., 2006). The accumulated sediments essentially originate from the
96 reworking of relict pro-deltaic lobes of the Rhone River and consist of materials directly eroded
97 from the massifs drained by the Rhone River and its tributaries. Several studies (BRGM, 2000;
98 Vassas et al., 2006) and more importantly the analyses of zircon typologies and apatite fission
99 track densities performed by Thomassin et al. (2007) demonstrated that the Alps and the Massif

100 Central are the two main sources for the heavy minerals that accumulate in the Camargue beach
101 placers.

102

103 **2.2. Separation of the mineral fractions**

104 Before analysis and mineral separation, the placer sand was washed, placed in an ultra-
105 sonic bath and oven-dried to remove organic material and seawater. Using heavy liquids
106 (bromoform and methylene iodide), the minerals were separated into three different fractions
107 according to their density. In the heaviest fraction ($d > 3.3 \text{ g.cm}^{-3}$), the main minerals were
108 isolated according to their magnetic susceptibility using a hand magnet and a Frantz Isodynamic
109 Magnet Separator. Due to their similar magnetic properties, monazite, epidote and titanite were
110 relatively difficult to separate from one another. However, the epidote and titanite grains were
111 generally larger than the monazite grains and we separated them by collecting the fine and
112 coarse fractions after simple $80\mu\text{m}$ -sieving. The isolated fractions were then purified by
113 handpicking under a binocular microscope. We obtained six pure mineral separates consisting
114 of garnet, ilmenite, rutile, zircon, epidote and monazite. However, due to the optical similarities
115 of ilmenite and magnetite and because it is impossible to completely eliminate impurities with
116 a hand magnet, we suspect that the pure ilmenite separate likely refers to a fraction containing
117 a few magnetite grains.

118 **2.3. Heavy mineral abundances**

119 Mineral proportions were determined under a binocular microscope in a fraction
120 containing all the heavy minerals isolated from the Camargue placer ($d > 2.9 \text{ g.cm}^{-3}$) using
121 standard optical characteristics such as grain colour or grain shape. In this heavy mineral
122 fraction, the mineral abundances were estimated as a percentage of the total counted grains.

123 As the identification of certain heavy minerals can be ambiguous in placers because of
124 altered or rounded grains, we also developed a method that uses micro X-ray fluorescence

125 mapping (μ XRF EDAX Eagle III) to quantify the mineral abundances in the heavy fraction (d
126 $> 2.9 \text{ g.cm}^{-3}$). Several hundred grains were analyzed by μ XRF in order to identify their spectral
127 signature and their mineralogical characteristics (see Supplementary File B). Then, using this
128 information, we calculated the relative abundance of each mineral species as a percentage of
129 the total grains analysed by μ XRF.

130 Combining the observations under the binocular microscope with the results obtained
131 by μ -XRF mapping, we estimated mineral abundances and converted them to mass percentage
132 using specific mineral densities and average grain sizes.

133

134 **2.4. Chemical analyses of the mineral fractions**

135 Trace element concentrations and Nd-Hf isotopic compositions were measured in bulk
136 fractions to evaluate the influence of each mineral on the geochemistry of the Camargue placer.
137 Measurements were performed on the six mineral separates (monazite, garnet, ilmenite, zircon,
138 epidote and rutile), the total placer and on two fractions, one containing all the light minerals
139 ($d < 2.9 \text{ g.cm}^{-3}$) and the other containing all the heavy minerals ($d > 2.9 \text{ g.cm}^{-3}$). To assess the
140 efficiency of the purification by handpicking under a binocular microscope, the impure
141 monazite, garnet, ilmenite and zircon fractions were also analysed.

142

143 *Sample dissolution*

144 The samples were first ground to fine powder by hand in an agate mortar to facilitate
145 dissolution. They were then dissolved by acid attack in steel PARR bombs for at least 2 weeks
146 at 135°C . Because of the well-known resistance of most placer minerals, we used sample-
147 specific dissolution procedures in which the sample quantity, the acid mixture and the
148 dissolution time in bombs were adapted to the mineral species (see Supplementary File C). In
149 addition, in order to improve the efficiency of the dissolution, acid-mixtures were regularly

150 removed from the bomb, stored in separated beakers and new acids were added every week.
151 After complete dissolution, two aliquots were taken from each dissolved sample, one to
152 measure trace element concentrations and the other for Nd-Hf isotopic compositions.

153

154 *Trace element concentrations*

155 Trace element concentrations were measured in mineral fractions using an Agilent
156 7500ce ICP-MS in Grenoble, France following a procedure similar to that published by Chauvel
157 et al. (2011). High precision measurements on ICP-MS were obtained by diluting samples in
158 2% HNO₃ with traces of HF at a specific dilution factor that depends on the sample and the
159 chemical element (see Supplementary File B). As described by Chauvel et al. (2011), ICP-MS
160 analytical drift was corrected by adding an internal standard (a multispikes containing Be, Ge,
161 In, Tm, Bi) to all samples. After correction for drift and oxide interferences, trace element
162 concentrations were calculated using an external calibration based on the repeated
163 measurements of the BR rock standard diluted 5000 times. To ensure the validity and the
164 reproducibility of our measurements, rock standards AGV-1 and BR 24 were measured several
165 times as unknown samples and several duplicates were performed (see Supplementary Table 2
166 and 3).

167

168 *Nd and Hf isotopic compositions*

169 Following the method described by Chauvel et al. (2011), Hf and Nd were isolated from
170 the same aliquot using ion exchange resins. For the pure mineral separates, the Hf isolation
171 procedure was slightly modified since the standard method was not suitable for minerals that
172 are much more concentrated in trace elements than usual rocks or sediments (see
173 Supplementary File B). The total procedural blanks were always less than 20 pg for Nd and 120
174 pg for Hf and can thus be considered as negligible relative to the amount of Nd and Hf present

175 in the samples. Nd and Hf isotopic ratios were measured on a Nu Plasma MC-ICP-MS at the
176 ENS Lyon, France. The mass fractionation bias was corrected using the constant values of the
177 ratios $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ and $^{179}\text{Hf}/^{177}\text{Hf}=0.7325$. Analytical drift was monitored by measuring the
178 Ames-Rennes Nd and Ames-Grenoble Hf standards every two or three samples and was
179 corrected using the recommended values published by Chauvel and Blichert-toft (2001) and
180 Chauvel et al. (2011). These two standards yielded a mean $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.511962 ± 13
181 (2σ , $n = 18$) and $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282160 ± 10 (2σ , $n = 11$).

182

183 **3. Results**

184 **3.1. Mineralogical composition of the heavy and light mineral fractions**

185 Using the weight of each separated fraction, we estimated that the light minerals ($d <$
186 2.9 g.cm^{-3}) represent only 5% wt of the total placer whereas the heavy minerals ($d > 2.9 \text{ g.cm}^{-3}$)
187 constitute about 95% wt of the sample. Observation of the light mineral fraction under the
188 binocular microscope shows that it mainly contains calcite, feldspar and quartz, but also a few
189 residual heavy minerals (ilmenite, zircon, etc...) that were not properly separated from the light
190 minerals by the heavy liquid separation procedure. Figure 2 shows the mineral abundances in
191 the heavy mineral fraction determined under the binocular microscope and using the μXRF
192 mapping. The mineral proportions estimated by combining the results from the two methods
193 are given in the grey-coloured inset as a percentage of the total counted grains and as a mass
194 percentage. The uncertainties on the mineral proportions and the details about mass percentage
195 calculations are given in the Figure caption. As shown in Figure 2, the results obtained by μXRF
196 mapping are remarkably consistent with the observations done under the binocular microscope.
197 The heavy mineral fraction mainly contains ilmenite-magnetite (44%) and garnet (28%) but
198 also significant proportions of zircon (10%), rutile (7%), monazite (3.5%) and epidote (2%).

199 The μ -XRF determination provides precise abundances when the minerals are present
200 in significant proportions (> 5%) and has the advantage to be quick and inexpensive. However,
201 when the analysed grains have complex spectral signatures with too many peaks or variable
202 proportions of chemical elements, as is the case for garnet and epidote, the method cannot
203 accurately identify and quantify mineral abundances. In such a case, observation under the
204 binocular microscope provides better results. Unfortunately, for ilmenite and magnetite, both
205 methods remain inefficient because the two minerals are optically similar and their μ -XRF
206 spectral signatures are highly variable depending on the degree of alteration (Nair et al., 2009;
207 Suresh-Babu et al., 1994), hence indistinguishable with μ -XRF. The ilmenite percentage
208 calculated in the heavy mineral fraction is probably overestimated because it includes some
209 magnetite.

210

211 **3.2. Trace-element concentrations**

212 Trace-element concentrations measured in the placer, in the pure mineral separates and
213 in the light and heavy mineral fractions are given in Table 1 and concentrations in the impure
214 fractions of monazite, garnet, ilmenite and zircon are given in Supplementary Table 3. Except
215 for garnet, the composition of the impure fractions is similar to that of the pure mineral separate
216 but generally less concentrated in trace elements. To compare the composition of the entire
217 placer with that of the pure mineral separates and the light and heavy mineral fractions, the
218 concentrations of REE and other trace elements were normalized to the average chondrite
219 composition of Evensen et al. (1978) in Figure 3a and to the average upper continental crust
220 values of McLennan (2001) in Figure 3b. Compared to chondrites, the REE enrichment factors
221 span several orders of magnitude from 10 to almost 400 000 (Figure 3a). All samples are
222 characterised by a negative Eu anomaly. Compared to upper continental crust, enrichment
223 factors range from about 0.01 to 4000 (Figure 3b) and almost all samples display significant

224 depletions in Cs, Rb, Ba, Sr and Li elements that are all known to be highly mobile during
225 alteration.

226 As can be seen in Figure 3b, trace-element concentrations measured in the total placer
227 are about 100 times those of upper continental crust and are quasi-similar to those of the heavy
228 mineral fraction. In contrast, the light mineral fraction has much lower trace element
229 concentrations, quite similar to upper continental crust values. These three fractions display the
230 same small negative anomalies in Nb, Ta and positive anomalies in Hf and Zr (Figure 3b).

231 Except for garnet, trace-element concentrations measured in the pure mineral separates
232 strongly resemble those published in the literature when available and/or are consistent with
233 partition coefficients determined in many studies.

- 234 • Monazite is extremely rich in Th-U and all REE but particularly the light REE (LREE)
235 (e.g. Kamineni et al., 1991; Ayres and Harris, 1997; Zhu and O’Nions, 1999; Nagy et
236 al., 2002; Thöni et al., 2008; Radulescu et al., 2009).
- 237 • Ilmenite is characterized by positive anomalies in Nb-Ta that are consistent with the
238 partition coefficients determined by Klemme et al. (2006) and Melluso et al. (2008) for
239 these two elements.
- 240 • Rutile and epidote display quite similar trace-element concentrations except for their
241 anomalies in Nb-Ta and in Zr-Hf which are positive for rutile and negative for epidote.
242 These features are in agreement with the partition coefficients determined by Foley et
243 al. (2000) and Klemme et al. (2005) for these four elements.
- 244 • Zircon differs from other minerals because of its strong depletion in LREE and its
245 significant enrichment in Hf and Zr (Figure 3; see Hoskin and Schaltegger, 2003 for a
246 review).
- 247 • Garnet is more enriched in HREE than in LREE (Figure 3a), displays unusual positive
248 Zr and Hf anomalies (Figure 3b) and its LREE concentrations are not as low as usually

249 measured in typical metamorphic or magmatic garnets (Jung and Hellebrand, 2006). In
250 the pure garnet separate, the higher LREE concentrations associated with the Hf and Zr
251 anomalies might be due to the presence of zircon inclusions and/or to an incomplete
252 sorting of the fraction.

253

254 **3.3. Nd and Hf isotopic compositions**

255 Nd and Hf isotopic ratios measured in the placer, the pure mineral separates and the
256 heavy and light mineral fractions are given in Table 2 and are plotted in a ϵ_{Hf} vs. ϵ_{Nd} diagram in
257 Figure 4. The isotopic compositions of the impure fractions of monazite, garnet, ilmenite and
258 zircon are given in Supplementary Table 3. Except for garnet, the compositions of the impure
259 separates resemble those of their respective pure mineral separates. Nd and Hf isotopic
260 compositions measured in the placer, the pure mineral separates and the heavy and light mineral
261 fractions span a large range of values from 0.512150 ($\epsilon_{\text{Nd}} = -9.4$) to 0.512594 ($\epsilon_{\text{Nd}} = -0.7$) for Nd
262 and from 0.282358 ($\epsilon_{\text{Hf}} = -15.1$) to 0.282942 ($\epsilon_{\text{Hf}} = +5.6$) for Hf. The pure zircon separate has
263 the highest Nd isotopic ratio and one of the lowest Hf isotopic ratios whereas the pure monazite
264 separate has the highest Hf isotopic ratio and one of the lowest Nd isotopic ratios. Considering
265 the analytical uncertainties on the measurements, the total placer, the rutile and the light and
266 heavy mineral fractions have similar Nd and Hf isotopic compositions which all lie on the
267 mantle array in the ϵ_{Hf} vs. ϵ_{Nd} diagram (Figure 4). Ilmenite and garnet have more radiogenic Nd
268 and Hf isotopic ratios that also fall on the mantle array in Figure 4. In contrast, epidote lies well
269 above the mantle array due to the radiogenic decay associated to its high Lu/Hf ratio.

270

271 **4. Discussion**

272 **4.1. Geochemical characteristics of the Camargue placer**

273 As heavy minerals are important carriers of trace elements (e.g. Götze and Lewis, 1994;
274 Preston et al., 2002; Totten and Hanan, 2007), we first decipher the contribution of each mineral
275 species to the overall chemistry of the Camargue placer in order to further investigate the Sm-
276 Nd and Lu-Hf systematics of beach placers.

277
278 *4.1.1. The heavy minerals control the trace element budget of the placer*

279 In Figure 5, we normalised the trace element concentrations of the heavy (high density,
280 $d > 2.9 \text{ g.cm}^{-3}$) and light (low density, $d < 2.9 \text{ g.cm}^{-3}$) mineral fractions to the bulk composition
281 of the Camargue placer to assess their respective contributions to the chemical budget of the
282 placer. The enrichment factors calculated for the heavy mineral fraction are very close to 1
283 whereas they are quite low for the light mineral fraction - usually < 0.1 . This clearly shows that
284 heavy minerals almost totally control the bulk geochemistry of the placer by hosting most trace
285 elements. Except for some mobile elements such as Cs, Rb, Ba, Sr and Li, the light minerals do
286 not sequester large amounts of trace elements. The very low concentrations measured in this
287 fraction indicate that it contributes to very little of the overall chemical budget of the placer but
288 it still has the potential to significantly dilute overall concentrations (Götze and Lewis, 1994;
289 Vervoort et al., 1999). We also see that the spectrum for the light mineral fraction in Figure 3b
290 is not really consistent with those usually found in the literature for quartz, feldspar or calcite,
291 the main mineral species present in this fraction (see Götze and Lewis, 1994; Govindaraju,
292 1994; Korotev, 1996; Monecke et al., 2000; Strnad et al., 2009). The light mineral fraction
293 displays unusual HFSE contents that strongly resemble those found in the heavy mineral
294 fraction (negative anomaly in Nb and Ta and positive anomaly in Zr and Hf, see Figure 3). This
295 feature is best explained by the presence of few heavy minerals in the light mineral fraction, a
296 feature not surprising since, unlike the pure mineral separates analysed in this study, the light
297 mineral fraction was not carefully purified by hand-picking under a binocular microscope.

298

299 *4.1.2. Trace elements hosted by pure mineral separates*

300 In Figure 5, the placer-normalised patterns reflect the contribution of each heavy mineral
301 to the bulk trace-element budget of the placer. With its very high concentrations, monazite
302 obviously is the major carrier of Th, U and REE. Zircon mainly controls Zr, Hf and to a lesser
303 extent U and HREE while rutile and ilmenite host most Nb and Ta in the placer. The other trace
304 elements such as Cs, Rb, Ba, Sr, Pb or Li are carried in variable proportions by several mineral
305 species and their concentrations in the total placer are not controlled by one or two specific
306 mineral species (Figure 5).

307 To ensure that we isolated and analysed all the heavy mineral species that significantly
308 contribute to the trace-element budget of the placer, we use the concentrations measured in the
309 pure mineral separates and the mineral proportions estimated as mass percentages in Figure 2
310 to calculate a theoretical trace element pattern for the heavy mineral fraction. In Figure 6, we
311 compare it to the measured values. We also take into account the uncertainties estimated on the
312 mineral proportions (see footnote of Figure 6 for more detail) and we model a field of variability
313 for the calculated heavy mineral fraction concentrations (blue field in Figure 6). With the
314 exception of the HREE and some mobile elements, our results show that the measured trace-
315 element pattern of the heavy mineral fraction is extremely well reproduced using the combined
316 proportions of pure monazite, zircon, ilmenite, garnet, rutile and epidote. This confirms that,
317 except for the HREE, the pure mineral separates account for the trace element budget of the
318 heavy mineral fraction. For Nd and Hf, our calculation shows that their concentrations in the
319 heavy mineral fraction are completely reproduced using only the mass proportions and contents
320 measured in the pure monazite and zircon separates. Other minerals play close to no role in the
321 overall abundance of Nd and Hf in the heavy mineral fraction. Monazite contains such high
322 amounts of LREE and zircon such high amounts of Zr and Hf that even though they constitute

323 only small percentages of the mineral assemblage, they are the controlling carriers of Nd and
324 Hf in the beach placer. Finally, we interpret the misfit between calculated and measured
325 concentrations for Cs, Rb, Ba and heavy REE (Figure 6) as being due to impurities in the garnet
326 separate and/or to the presence of a mineral such as titanite, which we did not separate and
327 analyse.

328 329 *4.1.3. What controls the Nd and Hf isotopic systematic of beach placer?*

330 Given that monazite and zircon are the carriers of Nd and Hf in the placer, they should
331 control the isotopic compositions. To confirm this hypothesis, we calculated a mixing curve
332 between these two minerals using the equation established by Faure (1977). This mixing curve
333 and the mass proportion of monazite in the binary mixture are shown in Figure 4. Because
334 monazite controls the Nd content and zircon the Hf content, the mixing hyperbola has such a
335 strong curvature that it resembles two perpendicular straight lines in the ϵ_{Hf} vs. ϵ_{Nd} diagram. The
336 first important observation is that, within uncertainties, the bulk composition of the placer, as
337 well as those of the light and heavy mineral fractions plot at the point of maximum curvature
338 on the mixing curve. A simple binary mixture of monazite and zircon without all the other
339 mineral species thus properly reproduces their Nd and Hf isotopic compositions. This confirms
340 that monazite totally controls the Nd isotopic composition in the placer as well as that of the
341 heavy and the light mineral fractions while zircon totally dominates the Hf isotopic
342 composition.

343 As a consequence of the concentration contrast between monazite and zircon for Nd and
344 Hf, the proportion of monazite in the monazite-zircon mixture varies widely near the point of
345 maximum curvature on the hyperbola (see the inset of Figure 4). Considering an uncertainty of
346 0.7 ϵ units on the isotopic compositions, mixing calculations demonstrate that as long as there
347 is 5 to 90% of monazite in the monazite-zircon mixture, the ϵ_{Nd} of the mixture remains similar

348 to that of the monazite and the ϵ_{Hf} to that of the zircon. A very wide range of monazite-zircon
349 ratio will thus produce Nd and Hf isotopic compositions that lie at the point of maximum
350 curvature on the mixing hyperbola. This, together with the fact that heavy mineral proportions
351 determined in the studied Camargue placer are comparable to those usually found in mature
352 beach placer deposits, make us very confident in the reproducibility of our results. Hence, we
353 are convinced that similar isotopic compositions would characterize placer samples taken from
354 various locations on the same beach even if heavy mineral proportions vary locally.

355 This latter observation potentially has major implications for beach-placer deposits in
356 other parts of the world. Indeed, monazite and zircon are very common minerals in most
357 coastal-marine placers (Patyk-Kara and Shevelev, 2000; Patyk-Kara, 2002) where they
358 represent 1-5 wt% and 5-20 wt% of the heavy mineral assemblage, respectively (e.g. Carpenter
359 and Carpenter, 1991; Force, 1991; Rao, 1994; Roy, 1999; Paine et al., 2005; Levchenko, 2006),
360 proportions that are comparable to those estimated in the Camargue placer. Given that zircon
361 is unequivocally the major carrier of Hf among common heavy minerals, we suggest that, as
362 for the Camargue placer, the Hf elemental and isotopic budget of worldwide beach placers is
363 likely entirely controlled by zircon. For Nd content and isotopic composition, the situation is
364 more ambiguous because the percentage of monazite in the heavy mineral assemblages can
365 sometimes be low and other minerals will influence the placer Nd isotopic composition if they
366 are present in sufficiently large proportions. Apatite probably constitutes the most serious
367 competitor to monazite in the REE budget of placers because it contains significant amounts of
368 REE and is sometimes present at the percent level in some beach placers. However, the normal
369 Nd content of monazite is at least 100 times that of typical apatite (see Ayres and Harris, 1997
370 and Belousova et al., 2002 for Nd concentrations in apatites) and 1000 times that of other
371 common placer minerals (cf Figure 3a; Götze and Lewis, 1994). A simple calculation shows
372 that even if a placer contains only 0.5% monazite, 5% apatite and 94.5% other minerals, 80%

373 of the overall Nd budget is still control by monazite. We therefore suggest that the Nd and Hf
374 isotopic compositions of worldwide beach placers should be controlled by monazite and zircon
375 even though their abundances in the heavy mineral assemblage are often low.

376 377 **4.2. Present-day Nd and Hf isotopic compositions of continental areas**

378 *4.2.1. The continental area drained by the Rhone River*

379 Previous studies showed clearly that the present-day Hf-Nd isotopic compositions of
380 crustal rocks plot on the extension of the mantle array in a Hf-Nd isotopic space and thus on
381 the same trend as rocks coming from the mantle (Vervoort and Patchett, 1996; Vervoort et al.,
382 1999; Vervoort et al., 2000) (Figure 4). In Figure 4, data for the Camargue placer lie on the
383 mantle array and also fall in the field of crustal rocks, suggesting that its present-day ϵ_{Nd} at -9
384 and its ϵ_{Hf} at -13 are quite comparable to that of continental crust materials. Our ϵ_{Hf} value is the
385 first published estimate for the Hf isotopic composition of crustal rocks from Western Europe
386 since no Hf data are available for the source rocks in the region drained by the Rhone River.
387 This is not the case for ϵ_{Nd} , however. Figure 7 shows that our ϵ_{Nd} value is identical to the average
388 value calculated from a compilation of ϵ_{Nd} reported in the literature for continental crust rocks –
389 granitoids and orthogneiss essentially – from the Massif Central and the Western and Central
390 Alps. It also corresponds to the average Nd isotopic composition of metamorphic rocks,
391 sediments and granitoids of the Hercynian fold belt of Central Europe (Liew and Hofmann,
392 1988). We conclude that the placer's Nd and Hf isotopic compositions represent those of the
393 average source region of the sediment, allowing us to provide the following estimate for the
394 Western European crust: $\epsilon_{Hf} \approx -13$ and $\epsilon_{Nd} \approx -9$.

395 396 *4.2.2. Can beach placers be used as proxies for other continental areas?*

397 While we believe that the Camargue placer might be a good proxy for the average Nd
398 and Hf isotopic composition of the continental area drained by the Rhone river, this might not
399 be the case for other beach placers. For an estimate based on placer data to be robust requires a
400 number of conditions that we will now examine. We demonstrated above that the Nd and Hf
401 isotopic compositions of the Camargue placer are controlled by monazite and zircon, ubiquitous
402 minerals that host most of the LREE and Hf in crustal rocks. However, it is also known that
403 parent/daughter ratios such as Sm/Nd and Lu/Hf change when minerals crystallize from a
404 magma (Faure, 1977) and that sedimentary rocks do not necessarily have the same ratios as
405 their sources (Patchett et al., 1984). As time passes after formation of the minerals, the isotopic
406 compositions of minerals evolve following their parent/daughter ratios, which might be
407 significantly different from those of the whole rock. The impact of the difference in
408 parent/daughter ratio needs therefore to be quantitatively evaluated before we can conclude that
409 placers represent proxies for the average Nd and Hf isotopic composition of their crustal
410 precursors.

411 In continental crust granitoids, Nd resides not only in monazite but also in other minerals
412 such as apatite, allanite or feldspar (Taylor and McLennan, 1995; Bea, 1996) that are not
413 systematically concentrated in beach placers when continental crust is eroded. Nevertheless, as
414 for most common granite-forming minerals (e.g. Taylor and McLennan, 1995; Bayon et al.,
415 2006), monazite has the same $^{147}\text{Sm}/^{144}\text{Nd}$ ratio as continental crust (see McLennan, 2001 and
416 Rudnick and Gao, 2003 for continental crust ratios and Ayres and Harris, 1997; Thöni et al.,
417 2008 and our own measurement for monazite ratios). Consequently, the monazite Nd isotopic
418 composition never significantly differs from that of crustal rocks and can be considered as a
419 good estimate of the average crustal value even if monazite does not dominate the Nd content
420 of crustal rocks. In contrast, most of the Hf in continental crust granitoids is hosted in resistant
421 zircons (Patchett et al., 1984; Candela, 2003), which have low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios compared to that

422 of continental crust (0.002 versus 0.013) (see McLennan, 2001 and Rudnick and Gao, 2003 for
423 continental crust ratios and Kinny and Maas, 2003 for zircon ratios). As a consequence,
424 significant isotopic differences develop between mineral and crustal precursor if the zircon
425 crystallization age is old. In practice, using a $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of 0.002 for the zircon and 0.013
426 for the continental crust, our calculations show that if the zircon crystallization age is younger
427 than 500 Ma, its isotopic composition differs from that of its crustal precursor by less than two
428 ϵ_{Hf} . This is simply because time is not sufficient for the difference in Lu/Hf to produce a Hf
429 isotopic composition in the zircon very different from that of the crust. As a result, the Hf
430 isotopic composition of a young zircon population, such as that in the Camargue placer, can be
431 considered as a valuable proxy for the average crustal value of the drained area. In the case of
432 an older zircon population, a correction could be applied provided that the average age of the
433 population is known.

434 In summary, we believe that placers have the potential to provide naturally averaged
435 information about the isotopic composition of large portions of the crust exposed to weathering
436 and erosion, information that is not always available as revealed by the numerous papers that
437 aim to estimate the composition of the continental crust (e.g. Taylor and McLennan, 1995;
438 McLennan, 2001; Rudnick and Gao, 2003). Although we recognize that analytical procedure,
439 particularly for sample dissolution, is sometimes difficult, we suggest that analyses of
440 worldwide beach placer deposits may constitute a fairly simple way to constrain the Nd-Hf
441 systematics of large continental areas. We recognize that this estimate does not take into
442 account mafic and ultramafic materials that could exist in the drainage area because monazite
443 and zircon, the two minerals controlling the Nd and Hf isotopic compositions of beach placers,
444 are not ubiquitous in mafic and ultramafic rocks. Beach placer deposits approximate therefore
445 the average isotopic composition of materials of continental affinity. Interesting sampling sites

446 could be the deltas of large rivers where vast amounts of terrigenous material are deposited and
447 where sea currents facilitate the formation of heavy mineral concentrates (Komar, 2007).

448

449 **4.3. Nd and Hf model ages of the drained continental area**

450 *4.3.1. Two stage model age calculations*

451 Since minerals do not necessarily have Sm/Nd and Lu/Hf ratios similar to those of their
452 whole rocks, Nd and Hf model ages of their crustal protolith must be calculated using a two
453 stage-model, a first stage for the time spent in the crust and a second for the evolution of the
454 mineral itself since crystallisation. For this calculation, we assume that the Sm-Nd and Lu-Hf
455 isotopic systems evolved first in a continental crust-type reservoir extracted from the depleted
456 mantle and then, after crystallisation, in the minerals themselves. An example of the calculation
457 for the Lu-Hf isotopic system is shown in Figure 8 and the calculated Hf model ages are shown
458 as a function of the Nd model ages in Figure 9. For the placer and for each mineral fraction,
459 model ages were estimated using a Monte-Carlo procedure to propagate uncertainties related to
460 (1) the isotopic composition of the depleted mantle (mean MORB-pole from the compilation
461 made by Chauvel et al., 2008), (2) the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of average continental crust
462 and (3) the crystallisation ages of the placer minerals (see caption of Figure 9 for more details).
463 As a primary hypothesis, we considered that the crystallisation age of all minerals were, on
464 average, Hercynian (300 ± 50 (2σ) Ma) given that (1) this period corresponds to the last major
465 magmatic event forming widespread plutonic bodies and occurring both in the Massif Central
466 Central and in the Western Alps (Pin and Duthou, 1990; Debon and Lemmet, 1999), the two
467 main sources of the placer minerals and (2) numerous studies have reported crystallisation ages
468 between 290 Ma and 340 Ma for monazite and zircon populations from the Massif Central and
469 the Western-Central Alps (e.g. Bossart et al., 1986; Sergeev et al., 1995; Bruguier et al., 2003;
470 Mezeme et al., 2006; Rossi et al., 2006; Gébelin et al., 2009). Using this assumption, similar

471 model ages are calculated for the two isotopic systems for the placer, the light and heavy
472 mineral fractions and for each pure mineral separate, as shown by the distribution in Figure 9.
473 In contrast, if we assume an average Alpine crystallisation age of about 30-50 Ma or any age
474 younger than 250 Ma or older than 350 Ma, large discrepancies occur between the Nd and Hf
475 model ages. This would imply a systematic decoupling of the Sm-Nd and Lu-Hf isotopic
476 systems in every mineral species, a situation that is obviously unrealistic. As an example for
477 the pure zircon separate, taking a crystallisation age of 50 Ma leads to Nd model ages (0.7 to 1
478 Ga) much younger than the Hf model ages (1.3 to 1.7 Ga) while taking a crystallisation age of
479 500 Ma provides Nd model ages (1.7 to 2.0 Ga) that are far older than the Hf model ages (1.2
480 to 1.5 Ga). We are therefore confident that calculating model ages using a mean crystallisation
481 age of 300 ± 50 (2σ) Ma for all the placer minerals provides robust information about the Nd
482 and Hf isotopic systematics of the source region. Note that the bulk placer and some of the
483 mineral fractions, such as the light and heavy mineral fractions, the pure ilmenite for Hf and
484 the pure rutile for Nd, have parent/daughter ratios that resemble those of the continental crust,
485 hence they have robust model ages that do not depend on the age of crystallisation we chose to
486 calculate them.

487

488 *4.3.2. Implications for the history of the drained continental area*

489 Almost all mineral fractions, and the placer itself, display consistent Nd and Hf model
490 ages (Figure 9) grouped around 1.4 - 1.5 Ga, suggesting that they derive from similar crustal
491 protoliths. The only exceptions are epidote and ilmenite both of which are characterised by
492 slightly younger ages around 1.1 to 1.3 Ga. Assuming a younger crystallisation age for these
493 two minerals does not significantly raise the Hf and Nd model ages. As a consequence, epidote
494 and ilmenite may record more recent geological events or their parent/daughter ratios may have
495 been disturbed by secondary processes.

496 Our calculated Nd and Hf model ages are fully consistent with the Proterozoic Nd model
497 ages reported for granitoids from the Massif Central and the Alps (e.g. Bossart et al., 1986;
498 Paquette et al., 1989; Downes et al., 1990) and strongly resemble those of metamorphic rocks,
499 sediments and granitoids from the European Hercynian fold belt whose model ages vary mainly
500 between 1.4 and 1.7 Ga (Liew and Hofmann, 1988). This suggests that the bulk composition of
501 the Camargue placer provides a true estimate of both the Nd and Hf model ages of the large
502 continental area drained by the Rhone River. More generally, Nd and Hf model ages obtained
503 on placer sands from continents could provide similar information for the crustal evolution of
504 large continental areas.

505 According to our measurements and calculations, the mean crustal residence age of the
506 Nd and Hf now residing in the Camargue placer minerals is Proterozoic, hence far older than
507 the age of the main orogenies that produced the Hercynian and Alpine terranes. As discussed
508 by many authors studying the Hercynian magmatism in the Massif Central and the Alps (e.g.
509 Bossart et al., 1986; Paquette et al., 1989; Pin and Duthou, 1990; Sergeev et al., 1995; Downes
510 et al., 1997), such model ages are best explained in terms of a two-component mixing between
511 new crust and an older component at least Early Proterozoic in age. This suggests strongly that
512 the main process occurring during the Hercynian and Alpine orogenies was reworking of old
513 continental crust with little addition of new material. Considering that the mean age of the old
514 crustal component is 1.8 - 2.0 Ga (Peucat et al., 1988) and that of the placer minerals is about
515 1.5 Ga, a simple calculation shows that a maximum of 20 - 30% juvenile crust could have been
516 added over the last 400 Ma i.e. during the recent Hercynian and Alpine events. Both Sm-Nd
517 and Lu-Hf isotopic systems thus record clear evidence that the continental area drained by the
518 Rhone River had a long history prior to the known Hercynian and Alpine events and that large
519 amounts of old crustal material with a mean Proterozoic age were reworked during the genesis
520 of rocks currently forming the Massif Central and the Alps.

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5. Conclusions

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This study provides the first analyses of Nd and Hf isotopes and associated trace element concentrations for a placer and the main mineral species it contains. Our results show that heavy minerals host most trace elements while light minerals only dilute concentrations. More specifically, we show that monazite and zircon control the Nd and Hf isotopic compositions, respectively, of the Camargue placer. A simple mixture of only these two minerals reproduces not only the isotopic compositions but also the Nd and Hf concentrations of the bulk placer. As the mass percentages of heavy minerals in the studied placer are typical of those commonly found in worldwide beach placer deposits, we suggest that monazite and zircon always dominate the Nd and Hf isotopic compositions of beach placer even though they are usually present in low proportions in the mineral assemblage.

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Our data indicate that present-day Nd-Hf isotopic compositions of the Camargue placer are representative of the crustal rocks found in the Massif Central and the Alps and provide therefore a reliable estimate of the average isotopic composition of the continental area drained by the Rhone River ($\epsilon_{Nd} \approx -9$, $\epsilon_{Hf} \approx -13$). The calculated Nd and Hf model ages for all placer minerals are consistent and provide an average Proterozoic age for the history of this part of the continental crust. We finally suggest that other beach placers formed at the mouths of large rivers in other parts of the world could provide reliable estimates of the average Nd-Hf compositions of other large continental areas, values that are usually not easy to obtain.

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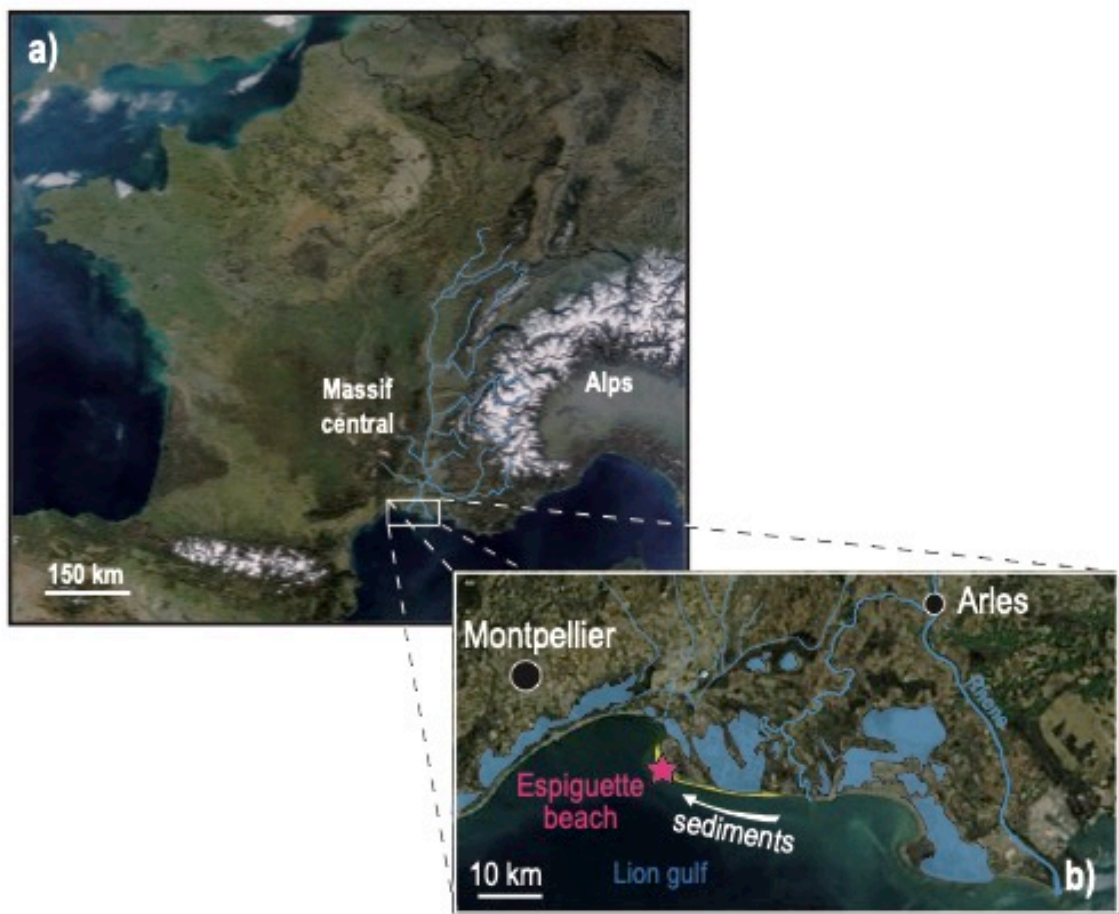
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815 **Figures**

816 **Figure 1: Location map of the studied area in France.** The massifs drained by the
817 Rhone river and its tributaries are indicated in map (a). The sampling site of the Camargue
818 placer and the sediment transport direction alongside the coast are shown in the inset (b).

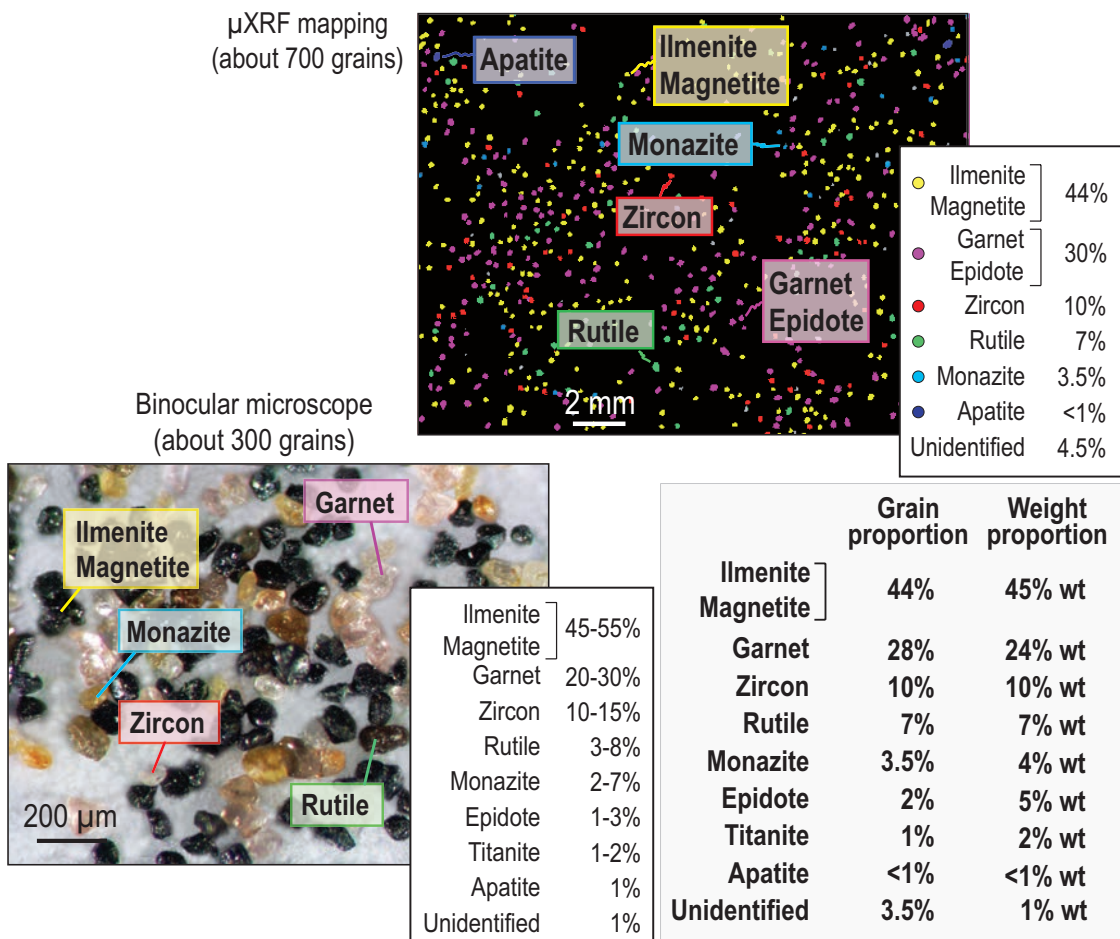
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Figure 1



821 **Figure 2: Mineral abundances in the heavy fraction (d>2.9).** A picture of the heavy
 822 fraction and the mineral proportions estimated as a percentage of the total grains counted under
 823 the binocular microscope are reported in the bottom left corner. The μ -XRF mapping showing
 824 the mineral species of the analysed grains on the adhesive surface and the mineral abundances
 825 calculated using this method as a percentage of the counted grains are presented in the top right
 826 corner. The heavy mineral abundances determined by combining the results from both methods
 827 are shown in the grey-coloured inset as a percentage of the total counted grains and as a mass
 828 percentage. For mass percentage calculations, we used the characteristic mineral densities given
 829 by Deer et al. (1992) and we estimated, based on binocular microscope observations, that all
 830 the grains had roughly the same volume except for the epidote and titanite for which the radius
 831 were considered to be 1.5 times larger than that of the other grains. Taking into account all
 832 sources of errors, the uncertainties on the mass percentages are estimated at about 3%.

833 **Figure 2**



835

Figure 3: REE and trace elements in the mineral fractions isolated from the

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Camargue placer. (a) REE patterns normalized to the average composition of chondrites as

837

given by Evensen et al. (1978). (b) Trace element patterns normalized to the average

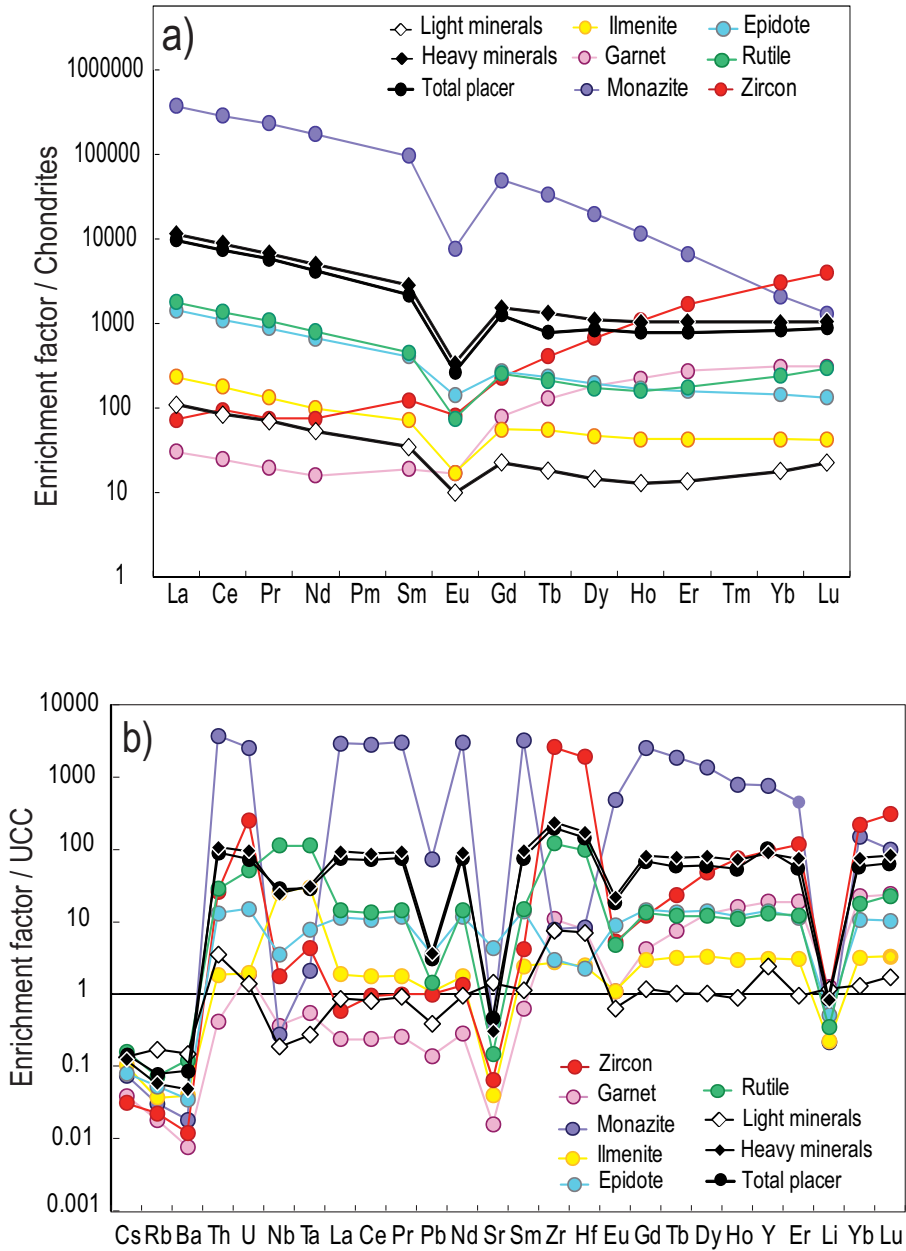
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composition of the upper continental crust given by McLennan (2001).

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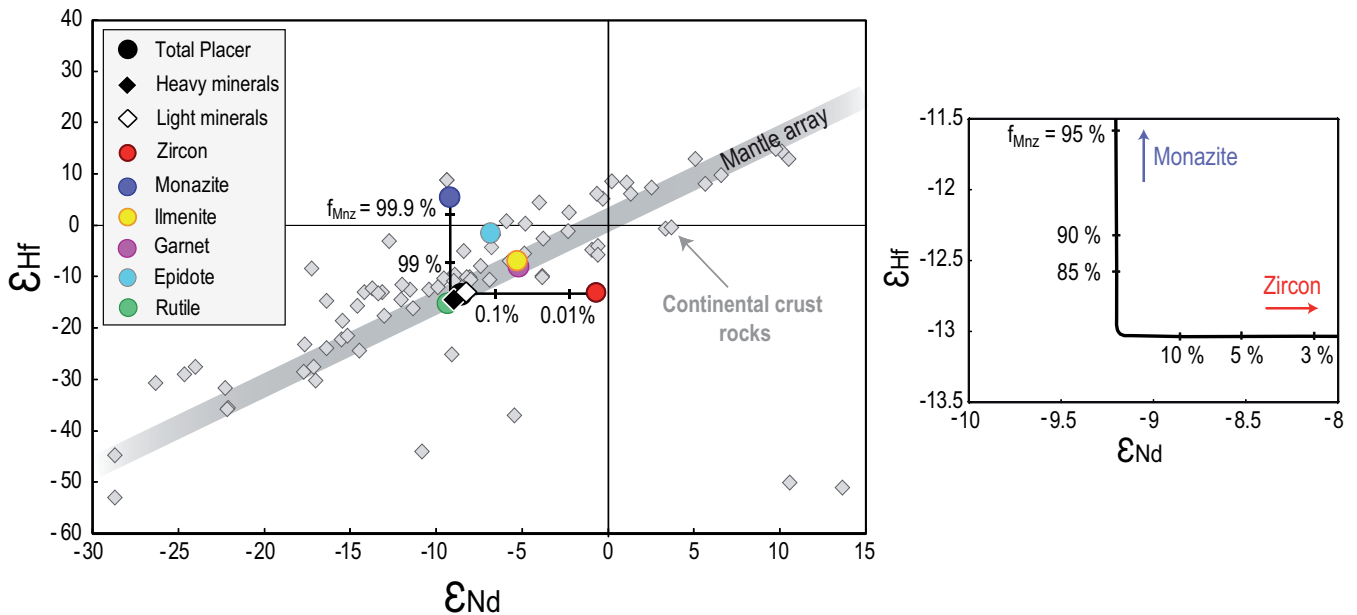
Figure 3

840



841 **Figure 4: Nd and Hf isotopes in the mineral fractions isolated from the Camargue**
 842 **placer.** The mantle array is that defined by Chauvel et al. (2008) associated with the CHUR
 843 composition given by Bouvier et al. (2008). The proportions of monazite (f_{Mnz}) in the binary
 844 mixing between zircon and monazite are shown by ticks on the mixing hyperbola connecting
 845 the two endmembers. The proportions of monazite in the point of maximum curvature of the
 846 mixing hyperbola are shown in more detail in the inset. Continental crust rock data are from
 847 Bennett et al. (1993), Vervoort et al. (1996), Vervoort and Patchett (1996), Vervoort and
 848 Blichert-Toft (1999) and Vervoort et al. (2000) and plot along an array of $\epsilon_{Hf} = 1.50 \times \epsilon_{Nd} - 0.60$.
 849 Note that this Nd-Hf relation has the same slope as the mantle array of Chauvel et al. (2008)
 850 but passes below the BSE value defined by Bouvier et al. (2008). Analytical errors are smaller
 851 than the symbol size.

852 Figure 4

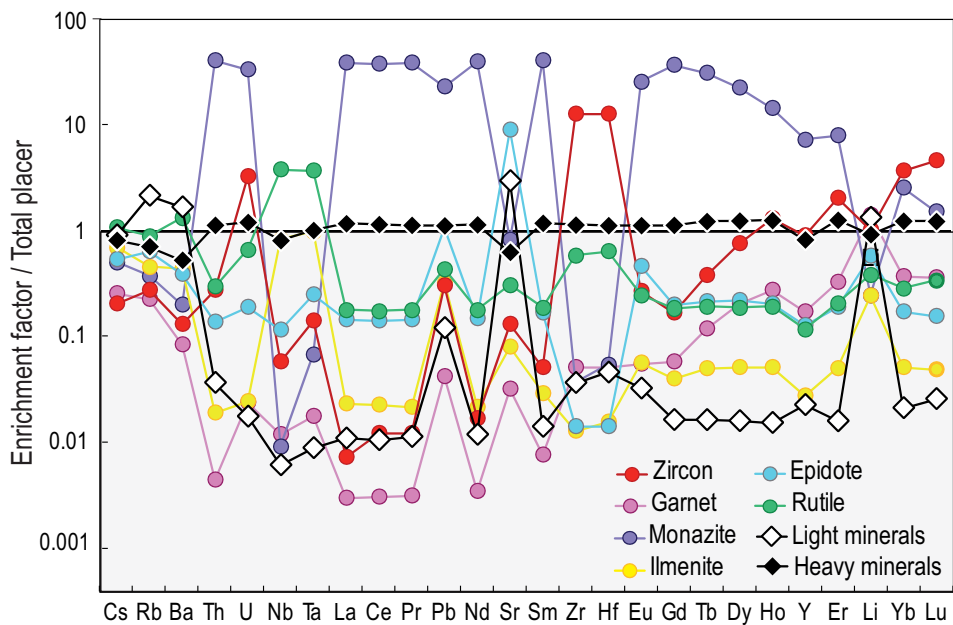


854 **Figure 5: Trace-element patterns of the mineral fractions normalised to the**
855 **composition of the Camargue placer.**

856

Figure 5

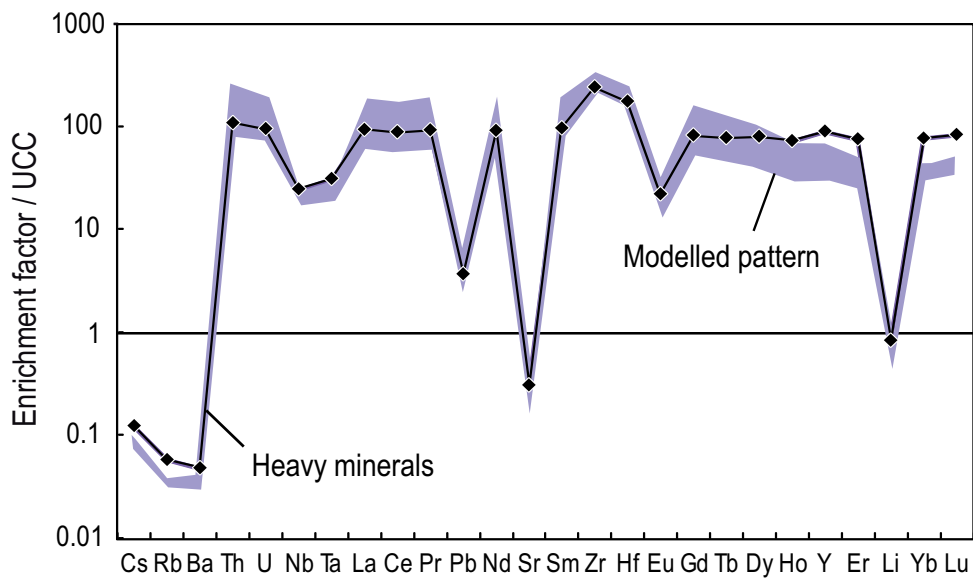
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858 **Figure 6: Modelling of the heavy-mineral trace-element pattern.** The concentrations
 859 in the heavy mineral fraction were modelled by summing the concentrations of the pure mineral
 860 separates multiplied by their mass proportions (estimates done under the binocular microscope
 861 and using the μ -XRF method for each mineral - see Figure 2). To take into account the
 862 uncertainties on mineral percentages, the proportion of the different phases was taken as
 863 variable within 2 limits: ilmenite + magnetite: 42 - 48 wt%, garnet: 21 - 27 wt%, zircon: 8 - 12
 864 wt%, rutile: 5 - 9 wt%, epidote: 3 - 7 wt% and monazite: 2 - 6 wt%. The blue field represents
 865 the entire range of modelled patterns obtained by sampling different mineral proportions within
 866 the ranges of values given above.

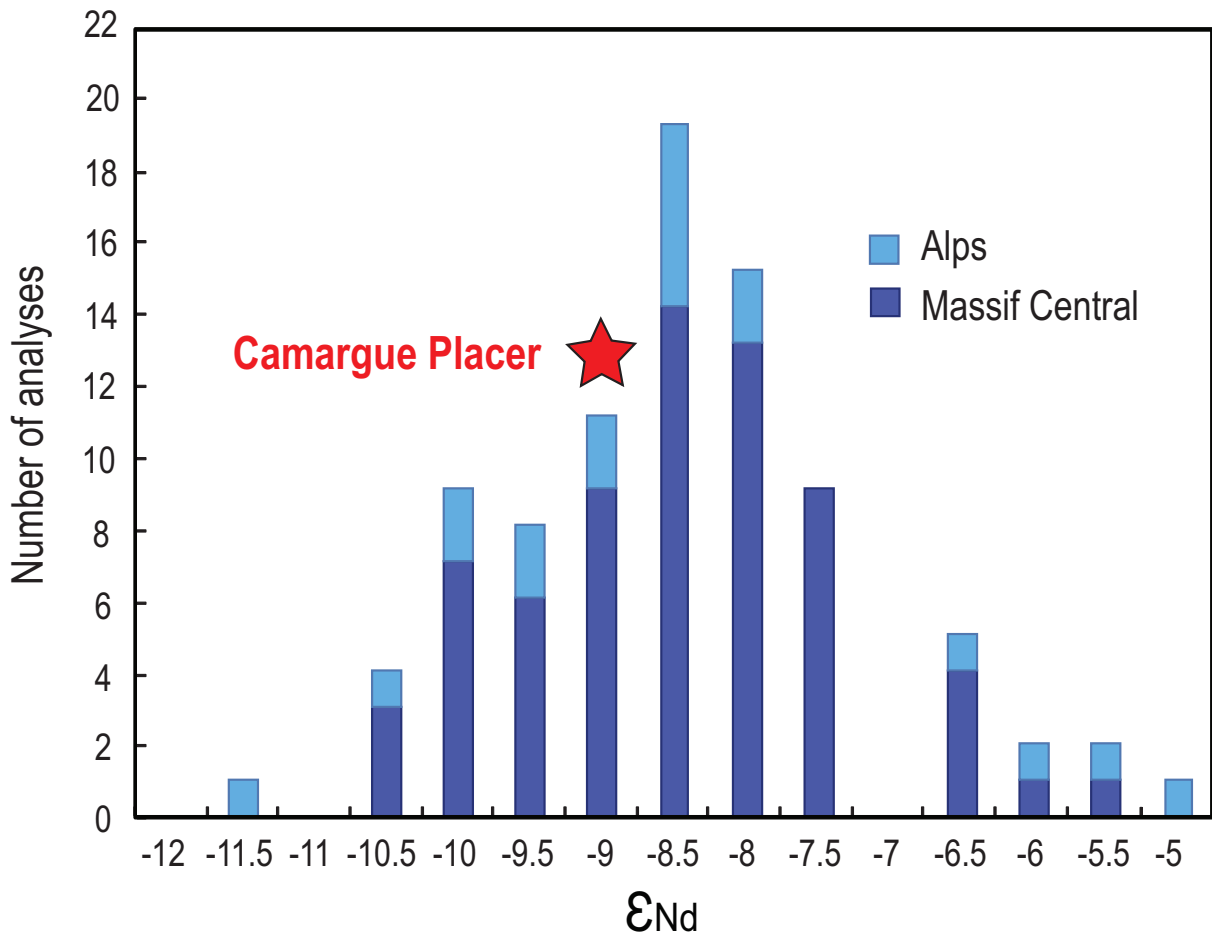
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868

Figure 6



869 **Figure 7: Histogram of ϵ_{Nd} values for crustal rocks from the Massif Central and the**
870 **Alps.** Whole-rock Nd isotope data are from Downes (1984), Bossard et al. (1986), Downes and
871 Duthou (1988), Paquette et al. (1989), Pin and Duthou (1990), Tilton et al. (1991), Downes et
872 al. (1997), Duchene et al. (1997), Henry et al. (1997) and Steinmann and Stille (2008). ϵ_{Nd} values
873 are calculated using the CHUR composition of Bouvier et al. (2008).

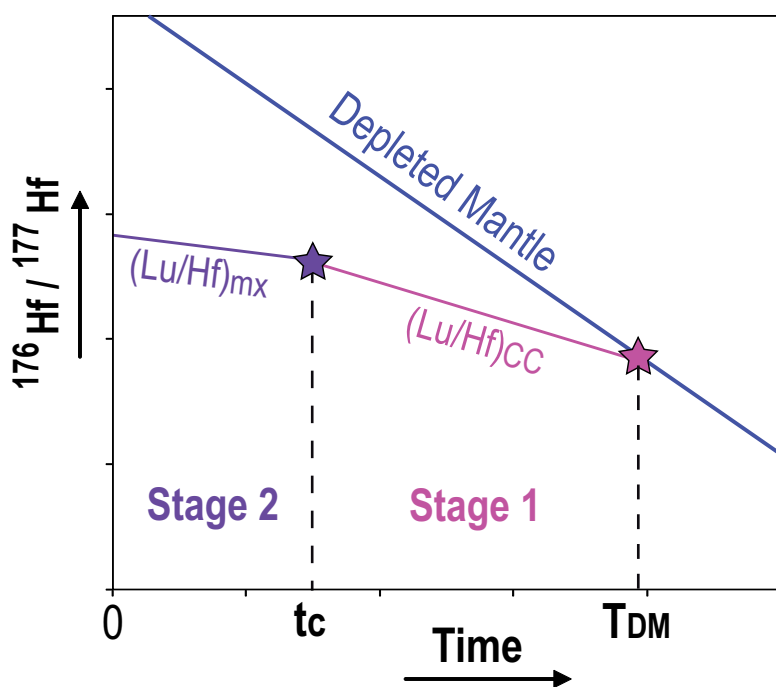
874 **Figure 7**



876 **Figure 8: Sketch of Hf two stage model age calculations.** CC: Continental crust. mx:
877 mineral. T_{DM} : Hf two stage model age (extraction time from the depleted mantle). t_c :
878 crystallisation age of the mineral.

879 **Figure 8**

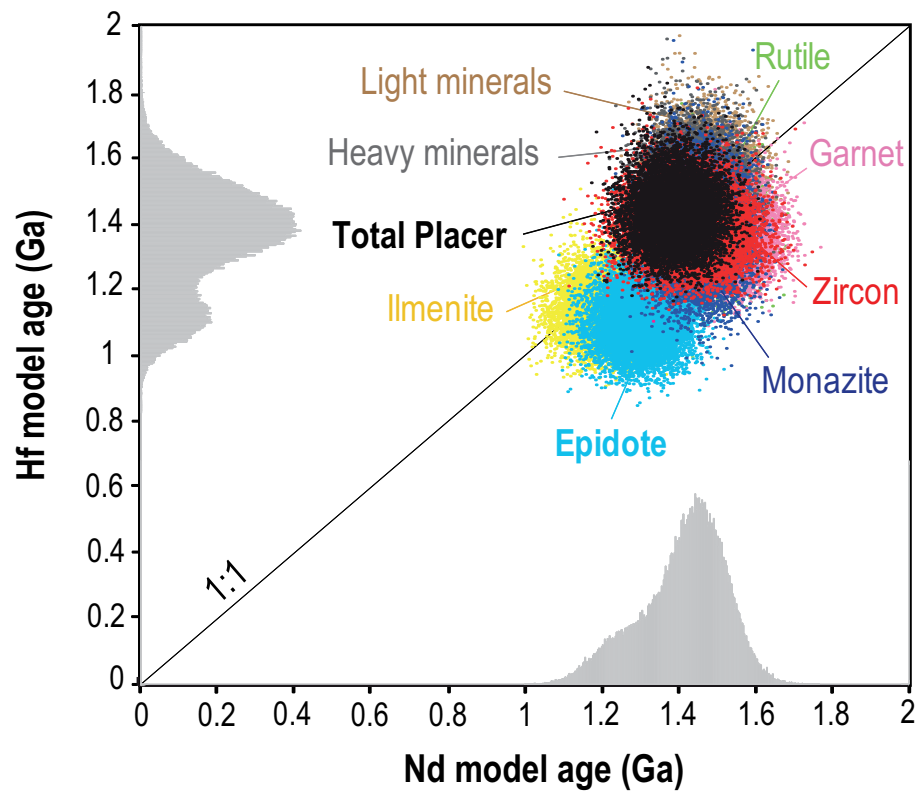
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881 **Figure 9: Hf model ages versus Nd model ages obtained from 10 000 Monte Carlo**
 882 **simulations.** As illustrated in Figure 8, model ages were calculated using two stages and the
 883 following equation (here for Hf):

$$884 \quad T_{DM} = t_c + \frac{1}{\lambda_{Hf}} \ln \left[\frac{\left(\frac{^{176}Hf}{^{177}Hf} \right)_{mx}^{t_c} - \left(\frac{^{176}Hf}{^{177}Hf} \right)_{DM}^{t_c}}{\left(\frac{^{176}Lu}{^{177}Hf} \right)_{CC}^{t_c} - \left(\frac{^{176}Lu}{^{177}Hf} \right)_{DM}^{t_c}} + 1 \right]$$

885 The acronyms used in this equation are similar to those of Figure 8. All the model ages
 886 were calculated using a Monte-Carlo procedure (n=10 000 for each mineral fraction and for the
 887 placer) to propagate the input parameter uncertainties. The distribution of crystallisation ages
 888 (t.) follows a Gaussian law with a mean value of 300 Ma and a standard deviation (2σ) of 50
 889 Ma. After having randomly sampled a crystallisation age in the latter distribution,
 890 $\left(\frac{^{143}Nd}{^{144}Nd} \right)_{DM}^{t_c}$, $\left(\frac{^{147}Sm}{^{144}Nd} \right)_{DM}^{t_c}$, $\left(\frac{^{176}Hf}{^{177}Hf} \right)_{DM}^{t_c}$ and $\left(\frac{^{176}Lu}{^{177}Hf} \right)_{DM}^{t_c}$ were calculated using the
 891 following parameters: (a) we assume that the depleted mantle has linearly evolved from a bulk
 892 Earth value at Earth formation, (b) we use the CHUR values published by Bouvier et al. (2008)
 893 and (c) we sample randomly the $\left(\frac{^{143}Nd}{^{144}Nd} \right)_{DM}^0$ and $\left(\frac{^{176}Hf}{^{177}Hf} \right)_{DM}^0$ isotopic ratios in Gaussian
 894 distributions centered at the mean-MORB pole of Chauvel et al. (2008) with a standard
 895 deviation (2σ) of 2ε units. $\left(\frac{^{143}Nd}{^{144}Nd} \right)_{mx}^{t_c}$ and $\left(\frac{^{176}Hf}{^{177}Hf} \right)_{mx}^{t_c}$ were calculated back in time
 896 using the Nd and Hf isotopic ratios and the Lu, Hf, Sm and Nd concentrations measured in this
 897 study. Finally, $\left(\frac{^{147}Sm}{^{144}Nd} \right)_{CC}^{t_c}$ and $\left(\frac{^{176}Lu}{^{177}Hf} \right)_{CC}^{t_c}$ were calculated using $\left(\frac{^{147}Sm}{^{144}Nd} \right)_{CC}^0$ and
 898 $\left(\frac{^{176}Lu}{^{177}Hf} \right)_{CC}^0$ ratios randomly sampled in Gaussian distributions centered at 0.115 ± 0.005 (2σ)
 899 and 0.013 ± 0.004 (2σ), respectively (values from McLennan, 2001 and Rudnick and Gao,
 900 2003). $\lambda_{Nd} = 6.54 * 10^{-12} \text{ yr}^{-1}$ and $\lambda_{Hf} = 1.87 * 10^{-11} \text{ yr}^{-1}$. For each mineral fraction and for the placer,
 901 colour dots show the location of model ages as calculated using the Monte Carlo simulation.
 902 The distribution of Nd and Hf model ages for all fractions together, are shown as histograms
 903 along the x and y axes.



905 **Tables**

906 ***Table 1: Trace-element concentrations measured in the various fractions (ppm).***

907 Concentrations were calibrated to the BR standard composition using the reference values
908 recommended by Eggins et al. (1997). Precision on the measured concentrations of most
909 elements is usually better than 5% as described in details by Chauvel et al. (2011) and values
910 obtained for the rock standards analysed as unknown samples are similar to published values
911 within 3% (see Supplementary Table 2).

912

913

Table 1: Trace-element concentrations measured in the various fractions (ppm)

Sample	CAM Mnz	CAM Grt	CAM Il	CAM Zr	CAM Ru	CAM Ep	CAM HMC	CAM fd NT	Plac7
Description	Monazite	Garnet	Ilménite	Zircon	Rutile	Epidote	Heavy minerals d > 2.9	Light minerals d < 2.9	Total placer
Li	4.49	25.6	4.45	18.4	7.04	10.5	16.7	24.2	17.9
Rb	3.48	2.09	4.22	2.53	8.23	5.95	6.53	19.9	9.09
Sr	143	5.6	14.1	23	53.5	1525	108	509	170
Y	17419	414	68.1	2137	285	313	1969	55.5	2363
Zr	1509	2090	528	501294	23353	581	45508	1494	39432
Nb	3.44	4.44	303	21.5	1366	42.7	295	2.29	360
Cs	0.356	0.181	0.489	0.145	0.749	0.379	0.572	0.643	0.694
Ba	10.3	4.32	22.5	6.7	67.2	19.7	26.7	85	50
La	90255	7.28	56.7	17.7	433	350	2788	26.7	2345
Ce	182339	15.4	113	60.6	866	699	5635	53	4833
Pr	22283	1.87	12.8	7.19	104	84.6	652	6.69	569
Nd	80352	7.42	46.2	35.2	374	312	2363	25.2	2039
Sm	14649	2.85	11	18.9	68.7	62.6	432	5.27	360
Eu	439	0.96	0.987	4.69	4.3	8.09	19.4	0.571	17
Gd	9927	16	11.3	59.9	52.9	55	324	4.66	271
Tb	1227	4.79	2.05	15.3	7.87	8.66	49.5	0.673	39.7
Dy	4968	46.1	11.7	171	42.8	49.4	279	3.66	221
Ho	656	12.7	2.4	60.1	8.9	9.6	58	0.725	45.5
Er	1081	44.6	7.09	276	28.6	26.5	173	2.23	135
Yb	344	50.6	7.05	495	39.1	23.6	168	2.94	134
Lu	33	7.78	1.07	99.5	7.38	3.37	26.6	0.569	21.3
Hf	50	47	14.6	11230	579	13.1	1012	42.2	889
Ta	2.14	0.549	30.2	4.4	113	7.8	31	0.28	30.3
Pb	1268	2.38	18.4	17.2	24.5	60.5	62.7	6.87	55.3
Th	40663	4.58	20.1	284	306	142	1154	38.2	1006
U	7233	5.33	5.54	720	146	42.4	265	3.96	217

914 **Table 2: Nd and Hf isotopic compositions of various fractions.** *Re-run* stands for run
915 duplicates. Uncertainties ($\pm 2\sigma$) reported in the Table correspond to in-run errors. Nd and Hf
916 isotopes were calculated relative to the Ames-Rennes Nd and Ames-Grenoble Hf standard
917 values given by Chauvel and Blichert-toft (2001) and Chauvel et al. (2011) ($^{143}\text{Nd}/^{144}\text{Nd} =$
918 0.511961 ± 13 (2σ) and $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160 \pm 12$ (2σ)). The reproducibility calculated using
919 re-run analyses and duplicates (see Supplementary Table 3) is 0.000013 (2σ , n=7) for the
920 $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and 0.000037 (2σ , n=7) for the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. ϵ_{Nd} and ϵ_{Hf} are calculated using
921 the CHUR composition given by Bouvier et al. (2008). Considering the reproducibility of the
922 entire analytical procedure, uncertainties are estimated at $\pm 0.7 \epsilon$ units for ϵ_{Nd} and ϵ_{Hf} values.

Table 2: Nd and Hf isotopic compositions of various fractions

Sample	Description	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2\sigma$	ϵ_{Nd}	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2\sigma$	ϵ_{Hf}
CAM Mnz	<i>Monazite</i>	0.512158	± 9	-9.2	0.282942	± 9	+5.6
CAM Mnz Re-run		0.512166	± 7	-9.0			
CAM Grt	<i>Garnet</i>	0.512363	± 9	-5.2	0.282559	± 6	-8.0
CAM II	<i>Ilmenite</i>	0.512359	± 8	-5.3	0.282593	± 7	-6.8
CAM II Re-run		0.512390	± 7	-4,7			
CAM Zr	<i>Zircon</i>	0.512594	± 5	-0.7	0.282417	± 5	-13.0
CAM Zr Re-run					0.282409	± 6	-13.3
CAM Ru	<i>Rutile</i>	0.512150	± 13	-9.4	0.282358	± 5	-15.1
CAM Ep	<i>Epidote</i>	0.512279	± 5	-6.9	0.282743	± 19	-1.5
CAM HMC	<i>Heavy minerals d>2,9</i>	0.512169	± 5	-9.0	0.282374	± 5	-14.5
CAM HMC Re-run		0.512183	± 9	-8,7	0.282378	± 6	-14.4
CAM fd NT	<i>Light minerals d<2,9</i>	0.512181	± 8	-8.8	0.282440	± 5	-12.2
CAM fd NT Re-run					0.282441	± 7	-12.2
Plac7	<i>Total placer</i>	0.512190	± 10	-8.6	0.282406	± 11	-13.4

Supplementary File A

Determination of heavy mineral abundances by micro X-ray fluorescence

Several hundred grains were laid down on an adhesive surface and mapped by micro X-ray fluorescence (μ XRF EDAX Eagle III) to identify spectral signatures that are characteristic for each mineralogical phase. The analyses were performed under primary vacuum with a $50\mu\text{m}$ X-ray spot size on a 512×400 pixel grid. Spectra were acquired on each pixel with a dwell time of 400 ms and a sampling step of $50\mu\text{m}$ in x and y. On the adhesive surface, the grains were previously spaced at distances of at least $50\mu\text{m}$ from each other to insure better recognition of the spectral signature of each grain. X-ray tube operating conditions were maintained at 20 kV and $200\mu\text{A}$ during all analyses. In the heavy mineral fraction ($d > 2.9$), the mineral species were discriminated using the X-ray fluorescence energies (K_{α} , K_{β} , L_{α} or L_{β}) of ten chemical elements (Si, Al, Ca, P, Zr, Ti, Fe, Mn, Nd and Ce) on a 0-20 KeV energy range. Among all spectra, we selected some representative reference spectra for the background noise and for each mineral of interest (ilmenite, magnetite, zircon, garnet, monazite and rutile). As used by Muñoz et al. (2008) for micro-XANES mapping, our computer code then determines the best linear combination of reference spectra that reproduces the intensities measured by μ XRF for the chosen chemical elements and for each pixel. If one of the linear coefficients is close to 1, the computer code associates the pixel with the corresponding mineral species (or the background); if not, the pixel is considered to be unidentified. Then, using this information and standard image processes, we created a map showing the nature of almost all the grains analysed by μ XRF and we calculate the relative abundance of each referenced mineral species as a percentage of the total grains analysed on the adhesive surface.

Supplementary File B

Sample dissolution

Because placer minerals are quite difficult to dissolve at 150°C in bombs, only few mg of each mineral fraction were dissolved in acid mixtures combining pure concentrated HF, HCl, HClO₄ and HNO₃ (see Table B.1). For the six pure and homogeneous mineral fractions, we dissolved the quantity required to measure both trace element concentrations and Nd-Hf isotopic ratios. In contrast, for the total placer and the two fractions of light and heavy minerals, we dissolved about 30 to 50 mg of powders to minimize heterogeneities and obtain representative analyses.

Trace element concentrations

To measure trace element concentrations similar to those of the BR rock standard (external calibration), samples were diluted about 5000 times before being analysed on the ICP-MS. In contrast, when trace element concentrations were unusually high compared to the BR rock standard (Hf in zircons, REE in monazites, etc...), high dilution factors were preferentially used to calculate precise concentrations (see Table B.1). In that case, the dilution procedure was performed in several steps by carefully weighing the mass of each aliquot taken from the “mother” solution. Several procedural duplicates were then analysed to evaluate the reproducibility of the entire dilution procedure.

Chemical separation of Hf in the pure mineral fractions

Even if the dissolved quantity of sample powder was initially low (few mg), our calculations show that the resin used for the second Hf column would be saturated if we loaded some of the pure mineral separates on a column filled with 2 mL of anionic resin. To avoid resin-saturation problems that may cause loss of Hf, the standard Hf isolation procedure

described by Blichert-toft et al. (1997) and modified by Chauvel et al. (2011) was adapted to each of the mineral fractions. For the rutile, monazite and zircon separates, the second Hf step that separates Hf from some major elements was removed because (1) these minerals do not contain high amount of these major elements and (2) there is a high risk to loose Hf during this step. For the epidote, garnet and ilmenite fractions, we kept the second Hf column because these minerals may contain significant amount of Fe, Ca or Al that need to be isolated from Hf to insure high precision on the Hf-isotope measurements (see Table B.1). However, to perform this step without saturating the resin, the ilmenite fraction was divided in two fractions loaded on two different columns that were subsequently merged to finish the chemical separation.

Table B.1 : Sample-specific analytical procedures

Sample	Description	Sample Dissolution			Trace element analyses	Hf isolation
		Dissolved Quantity	Acid mixtures	Time in bombs	Dilution factor	Second Hf column
Plac7	Total placer	≈ 50 mg	HF-HClO ₄ -HNO ₃	2 months	10000	x
CAM HMC	Heavy minerals	≈ 35 mg	HF-HClO ₄ -HCl-HNO ₃	2 months	500 000 for REE, U, Th, Y, Hf, Zr 5000 for the other elements	x
CAM fd NT	Light minerals	≈ 35 mg	HF-HClO ₄ -HNO ₃	1 month	5000	x
CAM Mnz	Monazite	≈ 35 mg	HF-HCl-HNO ₃	3 weeks	1 000 000 for REE, U, Th, Y 5000 for the other elements	
CAM Zr	Zircon	≈ 10 mg	HF-HClO ₄ -HCl-HNO ₃	2 months	5 000 000 for Hf and Zr 5000 for the other elements	
CAM Ru	Rutile	≈ 5 mg	HF-HClO ₄ -HNO ₃	3 weeks	5000	
CAM Il	Ilmenite	≈ 30 mg	HF-HClO ₄ -HCl-HNO ₃	3 weeks	5000	x
CAM Grt	Garnet	≈ 10 mg	HF-HClO ₄ -HCl	2 weeks	40 000 for REE 5000 for the other elements	x
CAM Ep	Epidote	≈ 5 mg	HF-HClO ₄ -HCl	2 weeks	5000	x

Supplementary Table 1: Heavy minerals identified in Espiguette black-sands (modified after BRGM, 2000)

Heavy minerals	Abundance	
Amphibole	L	R: Rare
Apatite	R	L: Low content
Biotite	R	A: Abundant
Carbonates	L	
Chlorite	R	
Disthene	R	
Epidote	A	
Garnet	A	
Ilmenite	L	
Iron hydroxides	L	
Leucoxene	R	
Magnetite	L	
Monazite	R	
Pyroxene	L	
Rutile	R	
Sillimanite	R	
Spinel	R	
Staurotide	R	
Titanite	R	
Tourmaline	R	
Zircon	R	

Supplementary Table 2: Trace-element concentrations in rock standards

	BR ref <i>Eggins et al.</i> (1997)	AGV-1 n=4	2 σ (%)	AGV-1 <i>Eggins et al.</i> (1997)	Diff (%)	BR 24 n=4	2 σ (%)	BR 24 <i>LGCA values</i>	Diff (%)
Li	14.9	11.0	0.8	11.2	2.0	7.17	1.6	7.06	-1.6
Rb	48.7	69.9	0.4	68.3	-2.4	84.6	1.2	83.67	-1.1
Sr	1364	674	1.2	655	-2.9	619	1.8	618.71	-0.1
Y	31.5	21.1	0.8	21	-0.5	30.9	0.6	30.96	0.2
Zr	283	244	1.3	240	-1.8	302	2.0	303.5	0.6
Nb	119	14.8	4.4	14.9	0.7	40.2	3.4	39.6	-1.5
Cs	0.823	1.31	2.2	1.31	-0.1	0.662	3.4	0.65	-1.9
Ba	1082	1220	3.4	1223	0.1	394	2.0	387.29	-1.7
La	82.1	38.4	0.8	38.5	0.2	34.0	0.8	33.43	-1.6
Ce	152	69.0	0.2	68.5	-0.7	73.3	1.6	72.66	-0.9
Pr	17.4	8.53	0.4	8.45	-0.9	9.63	1.4	9.59	-0.5
Nd	66.1	31.9	0.9	31.6	-1.1	39.8	1.4	39.67	-0.3
Sm	12.1	5.86	0.9	5.82	-0.6	8.33	2.2	8.33	0.0
Eu	3.58	1.59	3.0	1.57	-1.3	2.5	1.2	2.48	-0.7
Gd	9.57	4.62	1.8	4.73	2.3	7.41	1	7.32	-1.2
Tb	1.29	0.65	2.3	0.664	2.1	1.08	2.8	1.06	-1.5
Dy	6.3	3.53	2.9	3.54	0.2	5.68	1.8	5.67	-0.2
Ho	1.09	0.678	1.7	0.69	1.7	1.05	2.2	1.06	0.6
Er	2.59	1.84	3.1	1.86	0.8	2.72	1.2	2.71	-0.5
Tm									
Yb	1.81	1.63	1.3	1.64	0.8	2.09	0.4	2.09	-0.2
Lu	0.251	0.249	3.1	0.248	-0.3	0.303	3.4	0.3	-1.0
Hf	5.62	5.00	1.3	5	0.1	6.62	1.2	6.69	1.0
Ta	5.79	0.865	1.5	0.882	1.9	2.46	1	2.44	-0.9
Pb	4.77	37.5	1.1	37.3	-0.7	3.75	0.8	3.69	-1.7
Th	10.9	6.47	0.9	6.53	0.9	4.84	1.6	4.83	-0.1
U	2.46	1.9	1.7	1.89	-0.8	1.22	1.6	1.23	1.0

Standard deviations (2 σ) were calculated between the n measurement compositions of the two rock standards analysed as unknown samples and calibrated to the BR standard using the reference values given in the first column of this Table. Differences between the published values and our measurement compositions (Diff) are also reported.

Supplementary Table 3: Trace-element concentrations and Nd-Hf isotopic compositions of the impure fractions

Sample	CAM Mnz NT	CAM Mnz NT Re-run	CAM Grt NT	CAM Grt NT Dup	CAM Il NT	CAM Il NT Dup	CAM Zr NT	CAM Zr NT Re-run	CAM Zr NT Proc Dup
Description	Impure Monazites	Impure Monazites	Impure Garnets	Impure Garnets	Impure Ilmenites	Impure Ilmenites	Impure Zircons	Impure Zircons	Impure Zircons
Li	35.9		20.9	21.4	5.06		16.8		
Rb	10.3		3.47	3.3	4.16		2.97		
Sr	631		12.3	11.4	12.8		24.3		
Y	7038		359	359	33.9		1443		
Zr	1066		190	176	332		388303		
Nb	492		66.4	58.1	265		252		
Cs	1.62		0.369	0.382	0.474		0.188		
Ba	37.5		14.1	12.3	21.8		148		
La	33617		54.5	38.1	45		16.6		
Ce	69266		105	75.6	92.7		47.4		
Pr	8223		11.7	8.49	10.1		5.64		
Nd	29906		39.7	29.3	35.6		25.2		
Sm	5397		8.3	7.13	6.61		13		
Eu	201		1.19	1.16	0.592		3.47		
Gd	3513		17.8	18	5.62		34		
Tb	432		4.54	4.69	0.943		8.62		
Dy	1765		41.9	42.1	5.65		86.4		
Ho	232		11	11.1	1.18		46.2		
Er	421		38.5	38.6	3.68		207		
Yb	173		44.1	44.1	3.89		364		
Lu	19		6.79	6.76	0.613		73.5		
Hf	31.1		4.69	4.52	8.66		8818		
Ta	114		8.79	5.93	25.9		16.7		
Pb	422		16.7	14.6	18.5		15.4		
Th	34991		19	14.7	17.7		194		
U	2213		3.75	4.77	4.63		635		
143Nd/144Nd	0.512146	0.512158	0.512294	0.512350	0.512264	0.512274	0.512509		0.512505
± 2σ	± 6	± 6	± 7	± 8	± 8	± 6	± 5		± 6
εNd	-9.4	-9.2	-6.6	-5.5	-7.1	-6.9	-2.4		-2.4
176Hf/177Hf	0.282984		0.283656	0.283670	0.282582	0.282603	0.282375	0.282384	0.282382
± 2σ	± 22		± 15	± 8	± 7	± 12	± 7	± 6	± 7
εHf	7.0		30.8	31.3	-7.2	-6.4	-14.5	-14.2	-14.3

Trace-element concentrations (ppm) and Hf-Nd isotopic compositions measured in monazite, garnet, ilmenite and zircon fractions before their purification by handpicking under a binocular microscope. Concentrations were obtained in the same way as for their respective pure mineral separates. The two dissolutions of the impure garnet fraction are not very reproducible most probably because of sample heterogeneity (unpurified fraction with a complex mineral assemblage). **Dup**: dissolution duplicate. **Proc Dup**: analytical procedure duplicate. **Re-run**: run duplicate